Study of Molecular Trapping by Gold Nanofinger Arrays on Surface-Enhanced Raman Substrates

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14. ABSTRACT

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Study of Molecular Trapping by Gold Nanofinger

Arrays on Surface-Enhanced Raman Substrates

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  Abstract. The binding of *trans*-1,2-*bis*(4-pyridyl)-ethylene (BPE) molecules on substrates arrayed with gold nanofingers has been studied by surface enhanced Raman spectroscopy (SERS) and angle-resolved x-ray photoelectron spectroscopy (AR-XPS). Based on the SERS and XPS results, BPE molecules are found to interact with the gold nanofingers through the lone pair electrons of pyridyl nitrogens, not through delocalized π electrons. Furthermore, by comparing the AR-XPS spectra of finger arrays pre-closed before exposure to BPE with the spectra of arrays that closed after exposure to BPE, we observed at decreasing take-off angles, for which the surface sensitivity is enhanced, an increasing component of the nitrogen photoelectron peaks in the latter case which was associated with pyridyl nitrogen atoms residing on bridging sites. These results demonstrate that BPE molecules were trapped between the neighboring gold finger tips during the finger closing process. This resulted in a substantial increase in the SERS signal intensity since the self-limiting sub-nm gap between the fingertips is Raman hot spot.

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1. Introduction

Previously we reported a simple and yet easily scalable method to make flexible gold nanofinger arrays for SERS applications.[1] The high-density arrays of the gold nanofingers were fabricated over a large surface area using nanoimprint lithography (NIL). The high aspect ratio and the flexibility of nanofingers enable the arrays to undergo a self-closing process driven by micro-capillary forces during evaporation of the solvent, similar to processes that have been observed in analogous micro-scale structures.[2-4] We applied these nanofinger structures for SERS, and estimated the enhancement factor (EF) for *trans*-1,2-*bis*(4-pyridyl)ethylene (BPE) molecules located in the Raman hot spots to be $\sim 2 \times 10^{10}$. We speculated that the finger closing process might help to trap molecules between the finger tips and at the same time, incidentally create self-limiting sub-nm gaps that ensure the formation of Raman hot spots with a greatly amplified electromagnetic field under incident laser illumination. The contribution of sub-nm gaps to SERS enhancement has been studied both theoretically and experimentally[1, 5-7]; here we will focus on the experimental investigation of molecule trapping.

We examined nanofinger substrate surfaces exposed to BPE solutions with SERS and angle-resolved X-ray photoelectron spectroscopy (AR-XPS). Since BPE includes a highly delocalized π-electron system with chemically active pyridyl nitrogen atoms for binding to metal surfaces, it is widely employed as a stable probing molecule to evaluate SERS substrates[1, 8-10]. However, little has been reported regarding the bonding configuration of BPE on substrate surfaces. We present here not only the characterization of BPE bonding on our gold finger substrates, but also the verification of BPE trapping between the finger tips by using SERS and AR-XPS measurements.

2. Experimental section

Preparation of gold finger. As described in our previous report[1], the finger structures were fabricated using a combination of electron-beam lithography (EBL), reactive ion etching (RIE) and nanoimprint

lithography (NIL). Au with nominal thickness of 80 nm was deposited over the polymer fingers by e-beam evaporation. The typical diameter of each finger was 100 nm and the height was 750 nm.

SERS measurements. *Trans*-1,2-*bis*(4-pyridyl)-ethylene (BPE, Sigma-Aldrich, 97%) was diluted in ethanol at a concentration of 1 mM as a SERS analyte. To verify the molecule trapping between the closed finger tips, we compared two samples, that can be described as 1) BPE-trapped and 2) preclosed fingers. To prepare the BPE-trapped substrate, as-fabricated free-standing fingers were immersed in 1 mM BPE ethanolic solution for 10 min and then air-dried. For the preclosed fingers, the free-standing finger substrate was immersed in pure ethanol solvent and air-dried to induce irreversible finger closing, followed by re-immersion in the 1 mM BPE solution for 10 min and air-drying. Both samples were rinsed with pure ethanol before measurements. SERS measurements were performed using an upright confocal Raman microscope (Horiba Jobin YvonT64000) equipped with a nitrogen-cooled multichannel CCD detector. A 784.6 nm solid state laser was used as the excitation source with a measured power of 300 μW at sample surfaces. All spectra were collected with the same micro-Raman setup through a 100× objective lens and recorded in the range of 800–1700 cm^{-1} with 10 s accumulation time.

XPS Measurements and Analysis. X-ray photoelectron spectroscopy (XPS) measurements were performed using a monochromatized Al Kα source (hν=1486.7 eV, line width=0.25 eV), a hemispherical electron analyzer (Omicron, Sphera), and a multichannel detector under ultrahigh vacuum (UHV) conditions. The analyzer and x-ray source were configured at 90° relative to each other. The photoelectron take-off angles were set at 45°, 30°, 20°, and 10° with reference to the sample surface. To check sample stability, the spectra taken prior to and after a complete scan were compared. The binding energy (BE) for all spectra was calibrated to the Au $4f_{7/2}$ peak at 84.00 eV [11-13]. For the analysis of the spectra, peak component fitting (CasaXPS software) was performed using a Shirley background subtraction[14] and asymmetric Voigt functions (mixed Gaussian-Lorentzian), which were obtained from a multilayer BPE XPS spectrum. The fitting parameters were set to reduce the residual standard deviation (STD) of the measured and fitted XPS spectra. The multilayer BPE sample was prepared by repeatedly casting 10 M ethanolic BPE solution on a bare Si substrate and drying in air to form a thick BPE film (>

1000 μm). Charging in the multilayer sample was minimized by use of an electron flood gun during the measurement. The full width half maximum (FWHM) of the free pyridyl nitrogen components was fixed to 1.2 eV, which was the FWHM of the N 1s component obtained from the multilayer BPE sample.

3. Results and Discussion

Free-standing fingers as fabricated by NIL are shown in Figure 1a and in the SEM image of Figure 1c. After the open fingers were exposed to ethanol solution and blow-dried with N_2 gas, self-closing was observed, as shown in the schematic of Figure 1b and in the SEM image of Figure 1d. Using the solution with a target molecule, the flexible fingers may be brought together to trap molecules between the closed finger tips. In order to confirm the molecular trapping, two different samples (preclosed and BPE-trapped fingers) were prepared, as described in Figure 2. For the preclosed finger substrate (Figure 2a), the free-standing fingers were immersed in pure ethanol solution, followed by blow-dried with N_2 gas. After the irreversible formation of the closed fingers, the sample was re-immersed in 1 mM of ethanolic BPE solution for 10 min and air-dried. As shown in Figure 2b, the BPE-trapped fingers were prepared by immersion of the open fingers into the BPE solution followed by an air-dry.

We expect that for the BPE-trapped finger substrate, the BPE molecules are trapped between the finger tips, while the preclosed fingers may not have trapped molecules because binding sites between the finger tips are blocked. The schematic illustrations of magnified fingers tips in the preclosed and BPE-trapped samples are shown in Figure 2. As shown in the schematics, the amount of BPE molecules in the bridge sites is expected to be lower in the preclosed fingers than in the BPE-trapped fingers, while the bottom gold surface beneath the finger tips may be covered with a similar amount of BPE. Considering the molecular structure of BPE with two pyridine moieties and a vinyl group (Figure 2), we propose that the BPE molecules interact with a gold surface via either the pyridyl nitrogen[9, 15, 16] or the conjugated π electrons[16]. The two pyridine rings of BPE also allow two possible configurations: either a free-standing orientation involving binding via a single pyridyl nitrogen or a bridging configuration involving binding by both pyridyl nitrogens.

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The bonding configurations of BPE on gold have been investigated by comparing the Raman spectrum (Figure 3) of powder BPE and SERS spectra from preclosed and BPE-trapped fingers. The peak assignments are given in Table 1. The observed Raman spectra of the powder and adsorbed BPE are in good agreement with the reported spectra in the literature[9, 17, 18]. The peak at 994 cm^{-1} in the Raman spectrum of powder BPE (Figure 3a) was assigned to the ring breathing mode of BPE pyridine. This ring breathing mode includes the vibrational movement of the pyridyl nitrogen atom. It shows a blue-shift by 22 cm^{-1} and 25 cm^{-1} for the preclosed (Figure 3b) and BPE-trapped (Figure 3c) fingers, respectively. The peak observed at 1596 cm^{-1} in the powder spectrum is assigned to the C–N stretching mode of the pyridyl ring, which also includes the movement of the pyridyl nitrogen atom. This band undergoes a blue-shift of 12 cm^{-1} in the SERS spectrum of BPE-trapped fingers. The blue-shifted peaks in the finger spectra are all associated with the vibrational motions of pyridyl nitrogen, which indicates that the BPE molecules interact with gold via the pyridyl nitrogen atom. On the other hand, the bands at 880 cm^{-1} and 1635 cm^{-1} remain unshifted for the powder and finger samples. Both modes involve the vibration of the vinyl group within BPE. If the BPE molecule interacts with gold via π electrons, the conjugation between the aromatic ring and vinyl bond should be disrupted, resulting in a peak shift of the vinyl group. However, the Raman spectra show that this is not the case. Therefore, the BPE molecules must interact with gold via pyridyl nitrogen atoms, not π bonds. In addition, the BPE-trapped fingers exhibit a higher Raman intensity compared to the preclosed fingers, which is consistent with our previous study[1]. Comparing the BPE-trapped and preclosed fingers, the only difference between the two samples is most likely the existence of trapped BPE molecules between the finger tips. Therefore, we speculated that BPE molecule trapping between the finger tips might contribute to the higher Raman signal. However, one might equally argue that the preclosure of the fingers in ethanol blocks BPE adsorption sites on the surface of the gold fingers, and hence results in the lower Raman signal.

In order to settle this argument, we performed XPS measurements. High resolution N 1s XPS spectra were obtained at a take-off angle of 45° relative to the surface for three samples: the BPE multilayer (Figure 4a), the preclosed fingers (Figure 4b), and the BPE-trapped fingers (Figure 4c). All the N 1s

spectra were fitted using the same background and peak shape. The comparison of the total adsorbed BPE molecules for the BPE-trapped and preclosed finger was examined by integrating the N 1s peak relative to that of Au $4f_{7/2}$. The N/Au ratio was 0.063 and 0.064 for the BPE-trapped and preclosed finger, respectively, which suggests that roughly the same amount of BPE was adsorbed on both samples. The XPS spectrum of the BPE multilayer shows one peak at 398.7 eV, which is consistent with the reported N 1s XPS results of unmodified pyridine.[15, 19, 20]

As shown in Figure 4b and 4c, fitting of the N 1s XPS peaks yields three nitrogen components denoted as N1, N2, and N3. The N1 component in the spectra of the finger samples was observed at a binding energy (BE) of 398.7 eV, which is in perfect agreement with the peak position of N 1s peak for the multilayer sample. Based on the analysis of the BPE multilayer spectrum and previous studies[15, 19, 20], we assign the major component (N1) to the nitrogen of unmodified pyridine. Conjunction with our SERS results, the higher binding energy (BE) components, N2 and N3, can be assigned as pyridyl nitrogen atoms of BPE that have interacted with gold. A charge transfer from the lone pair electrons of the pyridyl nitrogen to the gold leads to higher BE of N 1s, which has been observed in previous studies[15, 19, 21-23]. The N2 component observed at 399.5 eV (0.8 eV higher than the N1 component) is generally assigned as weakly adsorbed pyridyl nitrogen on gold[19, 24-26]. The other component N3 was observed at 400.8 eV, which is typical for pyridyl nitrogens adsorbed on gold nanoparticles[19] and involved in strong H-bonding[15]. In one instance, a polymer with pyridyl groups coated with gold nanoparticles exhibited the pyridyl nitrogen at a BE of 400.7 eV.[19] Similarly, the strongly H-bonded pyridyl nitrogen has been observed around 400.7 eV.[15] We assign the N3 component to bridged BPE between finger tips or to BPE chemisorbed at one end to gold, which cannot be easily separated by peak-fitting. As compared to the weakly adsorbed configuration via one of pyridyl nitrogen atoms, the postively charged bridged nitrogen atoms at both ends of BPE can be less compensated by electron delocalization of highly conjugated π electrons since the electron delocalization is split between each pyridyl ring. This probably results in the higher BE of bridged nitrogen than the weakly adsorbed nitrogen. The peak-fitting results indicate that the fraction of the N3 component in the N 1s XPS peak

was 13% and 29% for the preclosed and BPE-trapped fingers, respectively. The fact that BPE-trapped fingers exhibit the larger amount of N3 suggests a scenario where the probability of the molecular trapping is greatly increased if the finger tips undergo closure during exposure to the BPE solution.

To further confirm the BPE trapping in the finger tips, we then performed angle-resolved XPS. Representative N 1s XPS spectra measured at four different take-off angles of 45°, 30°, 20°, and 10° relative to the surface are shown in Figure 5 for the preclosed and trapped samples. From the AR-XPS spectra, the fraction of the three nitrogen components was plotted for each take-off angle (Figure 6). For the BPE-trapped fingers, the decrease in the take-off angle resulted in a more pronounced N3 component. Since the measurement at a grazing angle provides higher surface sensitivity, the observation of increasing N3 signal with decreasing take-off angle shows that the bridged or strongly adsorbed BPE molecules are preferably located near the finger tips rather than uniformly distributed all over the finger surfaces. If the N3 component were mainly associated with strongly adsorbed nitrogen via only one of the pyridine rings, one would expect that the N1 component (free pyridyl nitrogen) should increase as the take-off angle decreases. The reduced N1 signal with decreasing take-off angle, as shown in Figure 6, shows that the increase of N3 is associated primarily with bridged BPE molecules. On the other hand, the preclosed fingers exhibit little change in the fraction of the N3 and other nitrogen components at decreasing take-off angles, which shows that the bonding configurations of BPE molecules on the preclosed fingers are similar everywhere on the substrate. Peak fitting results of the N 1s XPS spectra measured at a take-off angle of 10° are shown in Table 2. The N3 width for the preclosed finger (FWHM of 1.8 eV) is narrower than that for the BPE-trapped finger (FWHM of 2.6 eV). We interpret this observation to show that BPE is only chemisorbed via one nitrogen atom on the preclosed fingers, whereas it is present in both bridged and end-on configurations for the BPE-trapped substrate. While both species are believed to have roughly the same binding energy, small differences may still exist, and hence generate the broader peak width in the BPE-trapped sample.

4. Conclusions

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Trapping of *trans*-1,2-*bis*(4-pyridyl)-ethylene (BPE) on gold finger substrates was investigated by surface enhanced Raman spectroscopy (SERS) and angle-resolved x-ray photoelectron spectroscopy (AR-XPS). The results indicate that the BPE molecule interacts with the gold through the lone pair electrons of the pyridyl nitrogen, not through delocalized π electrons. The AR-XPS measurements further indicate that the BPE molecules can be trapped between the finger tips in a bridging configuration. The results confirm that active trapping of molecules can be achieved by the flexible gold nanofinger substrate and therefore lead to large and reproducible SERS enhancement.

FIGURE CAPTIONS

Figure 1. Self-closing of gold fingers; Schematic illustrations of (a) as-fabricated and (b) closed fingers; SEM images of (c) as-fabricated and (d) closed fingers.

Figure 2. Schematic illustrations of the preparation of preclosed and BPE-trapped gold fingers. The inset shows the magnified view of finger tips.

Figure 3. Raman spectrum of (a) powder BPE and SERS spectra of (b) preclosed, and (c) trapped-BPE fingers. The intensity of the powder spectrum was magnified 10 times.

Figure 4. N 1s high resolution XPS spectra of (a) BPE multilayer sample, (b) preclosed fingers and (c) BPE-trapped fingers. The data were obtained at 45° photoelectron take-off angle relative to the sample surface. Experimental spectra are shown as dots; solid lines represent best-fit curves; individual fitted components are shown as dashed lines. (N1: free nitrogen, N2: weakly adsorbed nitrogen, N3: bridged or strongly adsorbed nitrogen)

Figure 5. Angle-resolved XPS spectra of (a) preclosed and (b) BPE-trapped fingers. The take-off angles relative to the sample surface are shown in the spectra.

Figure 6. Fraction of three N 1s components as a function of take-off angle for the (a) preclosed and (b) BPE-trapped fingers. The integrated peak intensities of the N1 (white), N2 (light gray), and N3 (dark gray) observed in the AR-XPS spectra (Figure 5) were plotted as a function of take-off angle.

TABLES.

Table 1. Raman spectral peak assignment of powder BPE, preclosed finger, and BPE-trapped finger.

Table 2. Assignments and peak fitting results of the N 1s XPS spectra (Figure 5) obtained at the take-off angle of 10°.

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Figure 1.
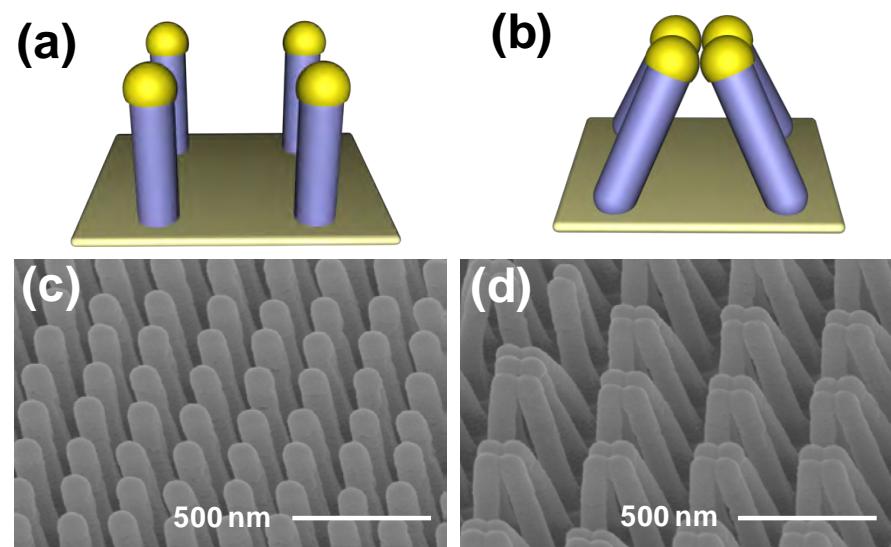
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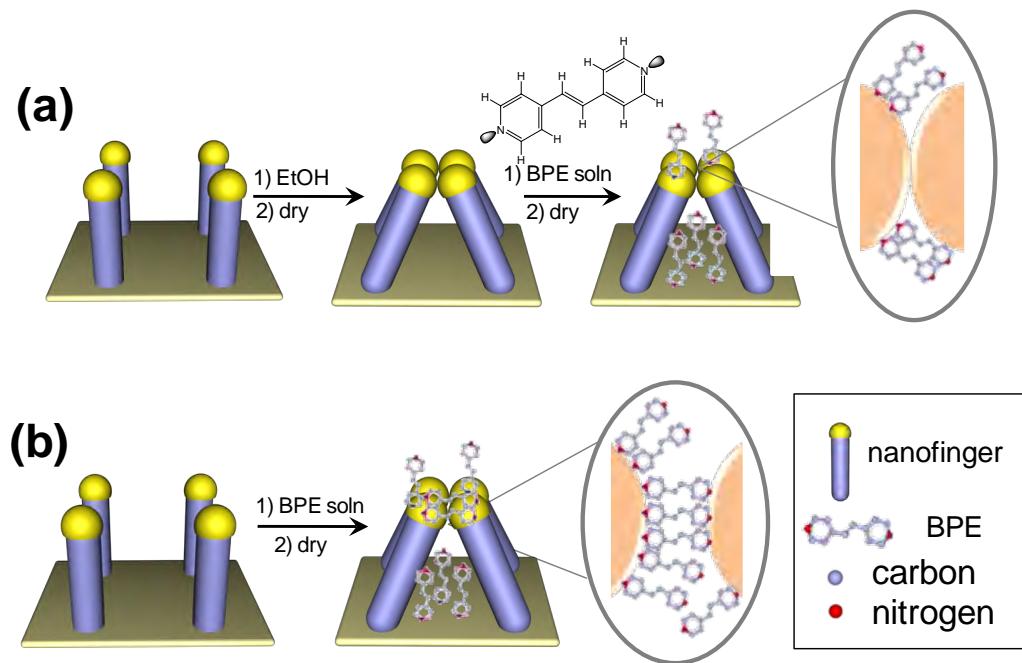
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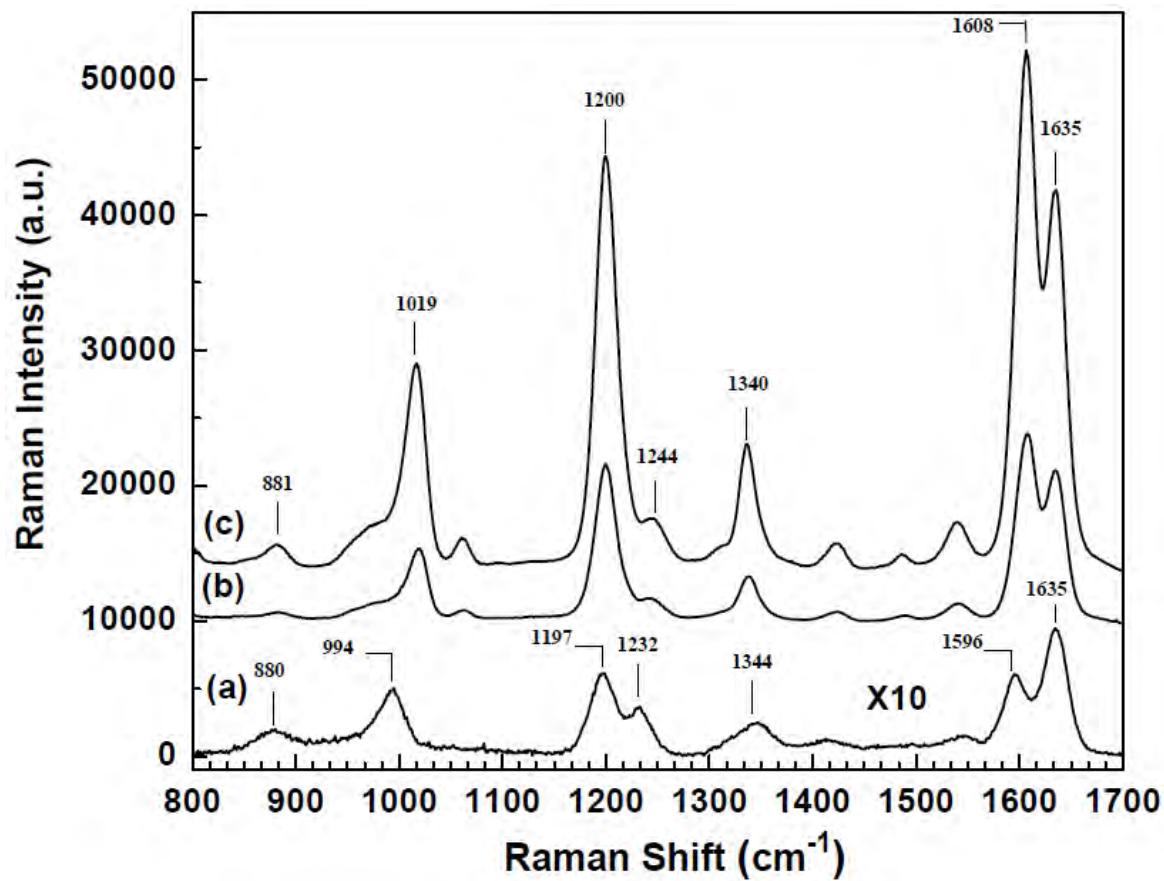
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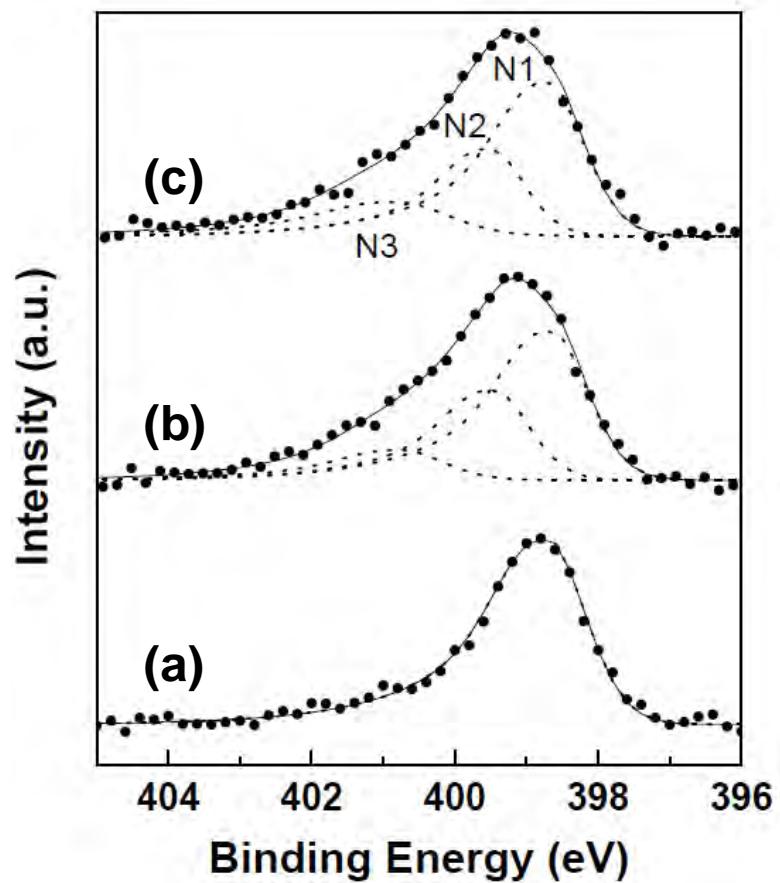
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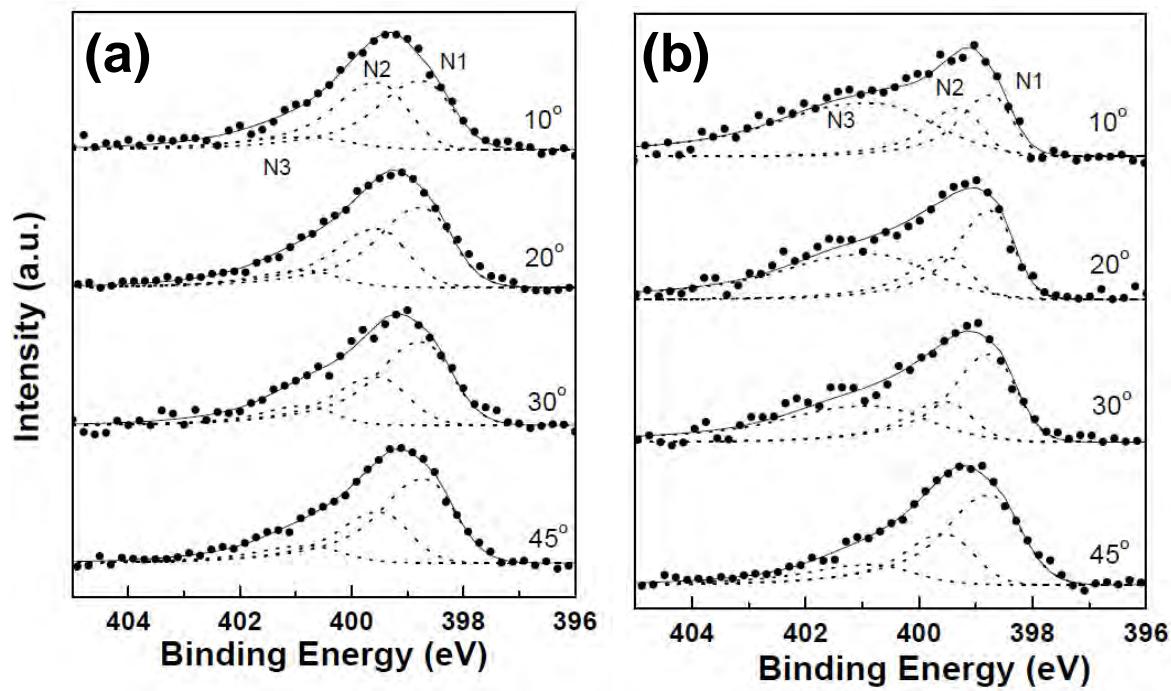
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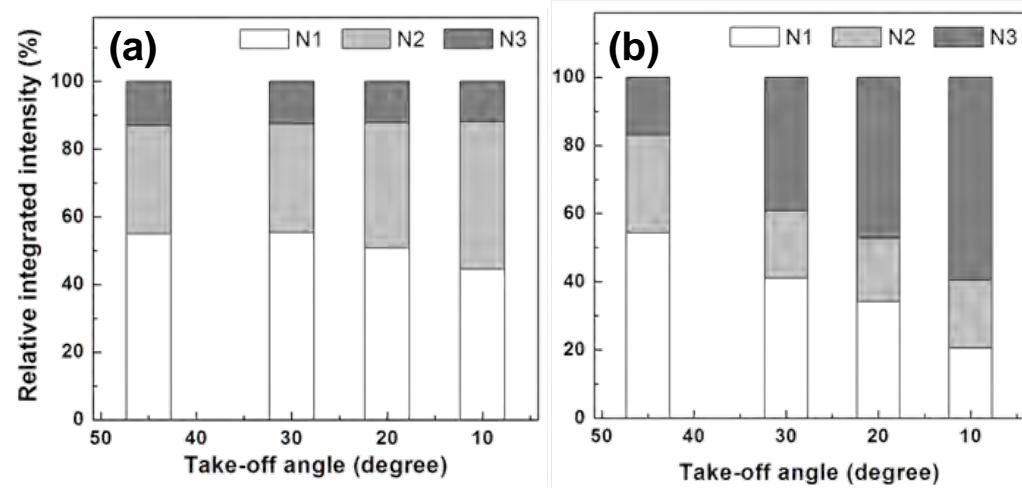
Table 1.

frequency (cm^{-1})			assignments
powder	preclosed finger	BPE-trapped finger	
880	881	881	δ(C=C)
994	1016	1019	ring breathing
1197	1200	1200	ν (C–C)$_{py}$, δ(C–N)$_{py}$
1232	1246	1244	δ(C–H)$_{py}$
1344	1339	1340	δ(C–H), δ(C=C)
1413	1422	1424	δ(C–H)$_{py}$
1546	1542	1542	ν (C–C)$_{py}$, δ(C–H)$_{py}$, δ(C–N)$_{py}$
1596	1607	1608	δ(C–N)$_{py}$, ν (C–C)$_{py}$
1635	1635	1635	ν (C=C)

Table 2.

	suggested assignment	Preclosed finger			BPE-trapped finger		
		BE (eV)	relative intensity	FWHM (eV)	BE (eV)	relative intensity	FWHM (eV)
N1	free nitrogen	398.7	45%	1.2	398.7	21%	1.2
N2	weakly adsorbed nitrogen	399.5	43%	1.2	399.3	19%	1.2
N3	bridged or strongly adsorbed nitrogen	400.8	12%	1.8	400.8	60%	2.6

molecule trapping?